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A study of electrode glow during electrolysis

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[Plates—3A-3B and 4A-4B]

Electrode glows during the electrolysis of aqueous alkali solutions at wire electrodes of different materials and dimensions have been studied using spectroscopic and oscilloscopic techniques. It has been shown that the glow does not depend upon the electrolyte but is governed mainly by the electrode geometry. The glow spectrum consists of the atomic lines of the electrode material and the metal ions in the electrolyte along with some band structures in the case of the cathode glows. The anode glow spectrum exhibits a few atomic lines of the alkali metal ions, superimposed on a continuum. It is proposed that these glows are due to corona discharges through an insulating thermal layer surrounding the electrode. The nature of this layer is essentially similar to the thermal boundary layer encountered in the electro-hydro-dynamic (EHD) techniques The onset of the glow is primarily governed by the dimensions of the insulating layer, the temperature of the electrolyte and the field distribution around the layer. The oscillographic studies have revealed corona discharge pulses in the insulating layer surrounding the electrodes.

Introduction

Following the interesting work on electrode glow during electrolysis, recently reported by Palit (1967), the authors have undertaken detailed investigation of this phenomenon in order to study the conditions under which this glow appears and to understand the basic mechanism of the glow process. Preliminary results of this work have already been reported earlier (Mande & Edkie 1961).

According to Hickling & Ingram (1964) this phenomenon was probably first observed at a platinum electrode during the electrolysis of water by Fizeau & Foucault as early as in the year 1854. These authors, who observed that the glow was particularly intense at the cathode, considered it to be an arc discharge through hydrogen. In the year 1950, Kellogg, using higher current densities in aqueous solutions observed intense glows at wire electrodes and attributed them to local heating. He also pointed out the similarity between this phenomenon and the well known anode effect observed in the electrolysis of fused salts. More recently, Hickling & Ingram (1964) have studied this phenomenon in detail, particularly the reactions at the anode and the corresponding power requirement for the production of a continuous glow. According to Ivey (1963) the glow in aqueous solutions can be termed as 'galvano-luminescence'. Kuwana (1966) has recently given an historical account of this type of work with particular reference to origanic electrolytes. Very recently Palit (1968) has studied the liberation

of hydrogen and oxygen together on the electrodes during electrolysis accompanied by electrode glow in a number of electrolytes. As no spectroscopic and oscilloscopic investigations of this phenomenon in alkali solution appear to have been reported so far, it was thought worthwhile to undertake this study.

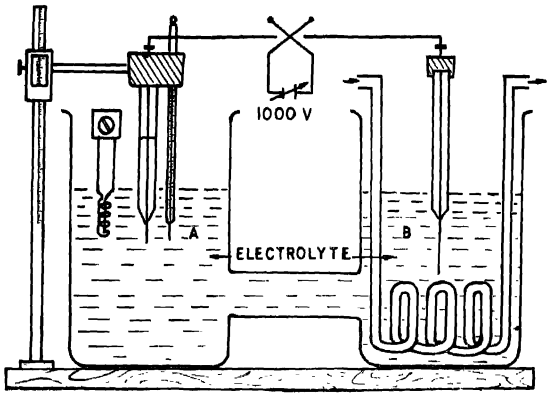


Figure 1. Basic experimental set up.

Experimental

The main experimental arrangement used in this investigation is shown in figure 1. It essentially consists of two beakers, each of 500 c. c. capacity, joined together by a glass tube of 1. 5 cm internal diameter. The region *A* of the electrolyte could be heated by using an immersion heater and the region *B* could be cooled by using a water-cooled copper coil. A sufficient temperature difference between the two regions *A* and *B* surrounding the electrodes could be maintained by using this arrangement. Different types of electrodes, such as, platinum and tungsten wires fused in glass and thin copper and aluminium rods, introduced through suitable glass tubes into the electrolyte, were tried. The power for the electrolysis was obtained from a D. C. power supply unit, fabricated in this laboratory, giving upto 1000 volts at 2 amps. The depth of immersion of the electrodes in the electrolyte could be adjusted with the adjustable stands for the electrodes. This was necessary in order to compensate for the changes in the electrolyte level caused by heating effects.

Spectrosopic investigations of glow at low dispersion were carried out on a constant deviation glass prism spectrograph manufactured

by the Andhra Scientific Co., India. In order to obtain more details, the spectra were also photographed on Hilger medium quartz spectrograph. Since the glows were flickering it became necessary to use rather wide slits to record the glow spectra. Iron arc and hydrogen discharge tube spectra were recorded for comparision, using Hartmann 3-aperture diaphram. The slit width, exposure time and the power supply for the production of the glow were suitably adjusted in each case.

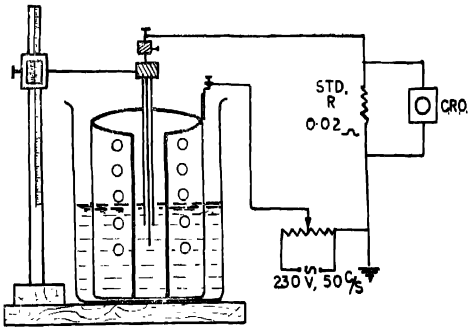


Figure 2. Experimental set up for oscillographic studies.

It was found difficult to lock-up the random pulse pattern causing the glow on a cathode ray oscillograph under purely D. C. conditions. These difficulties were minimized by using a modified experimental arrangement as shown in figure 2. A hollow, slotted, stainless steel cylinder of diameter 6 cm and height 8 cm and a thin axially placed wire within the cylinder served as electrodes. The power for the electrolysis was obtained from A. C. mains through a variac. A Hewlett-Packard C. R. O. was connected across a standard low resistance, *R*. The oscillographic traces were photographed using the camera attachment of the C. R. O.

Results

The results obtained in this investigation are described in the following there sections :—

I. Effects of the concentration and temperature of the electrolyte and the geometry of the electrodes on the glow.

II. Spectroscopic studies of the glow.

III. Oscillographic studies of the glow.

I(a). *Effect of concentration of the electrolyte*

In this investigation platinum wires were used as electrodes ; one of them was of diameter 0.5mm and length 2.0 cm and the other was of diameter 0.15mm and length 0.72cm. $CaCl_2$ and NaOH solutions of different concentrations, in the range 0.0027 to 0.20 molar, were used as electrolytes. The depth of immersion of the thinner electrode in the electrolyte was maintained at 3.0cm from the free surface.

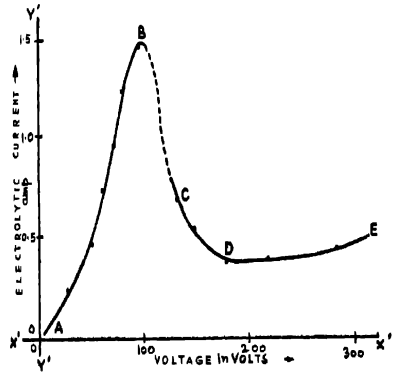


Figure 3. Variation of current with applied voltage in the cell circuit.

It was observed that as the potential difference between the electrodes is gradually increased, at a certain critical voltage the current suddenly decreases with fluctuations. A large number of bubbles are then seen to surround the electrodes and a spectacular glow, surrounding the thinner electrode, appears. By changing the polarity of the electrodes, it was found that the glow always appears at the thinner electrode, irrespective of its being either the cathode or the anode. By changing the concentration of the electrolyte it was observed that the concentration has very little effect upon the input power required to produce a continuous glow. A curve showing the variation of the electrolytic current with the applied voltage for 0.1M $CaCl_2$ solution is shown in figure 3. The general nature of the curves for different concentrations of the electrolytes is essentially similar. The point D on the curve, shown in figure 3, indicates the onset of the continuous glow at the thinner electrode. Table 1 gives the power requirement for the onset of the continuous glow during the electrolysis of $CaCl_2$ and NaOH solutions of different concentrations.

TABLE 1. POWER REQUIREMENT FOR A CONTINUOUS GLOW, CORRESPONDING TO THE POINT '*D*' ON THE CURVE IN FIGURE 3, AT A PLATINUM CATHODE OF DIAMETER 0.15mm AND LENGTH 0.72cm.

Concenrration	Volts (for $CaCl_2$)	Amps	Watts	Volts (for NaOH)	Amps	Watts
0.0027M	250	0.29	72.5	150	0.47	70.5
0.004M	235	0.30	68.9	145	0.48	69.6
0.010M	215	0.32	68.8	135	0.51	68.9
0.050M	205	0.34	69.7	128	0.53	67.8
0.100M	190	0.37	70 3	120	0.57	68.4
0.200M	170	0.40	68.0	108	0.62	66.9

I(b). *Effect of temperature*

Using the same electrode system as described in the earlier section, it was found that as the temperature of the region *A* surrounding the thinner electrode is gradually increased, keeping the temperature of the region *B* constant at about 35°C, the input power required for the appearance of the continuous glow goes on decreasing. When the temperature of the region *A* approaches about 99°C, the input power required for the glow is found to be almost negligible.

I(c). *Effect of the geometry of the electrodes*

In this investigation three sets of platinum wire electrodes were used. The first set consisted of one wire of diameter 0.5 mm and length 2.0 cm and the other of diameter 0.15 mm and length 0.72 cm ; the second set consisted of one wire of diameter 0.3 mm and length 1.0 cm and the other of diameter 0.15 mm and length 0.59 cm ; the third set consisted of both the wires of diameter 0.15 mm and length 1.5 cm. It was found that the glow always appears at the thinner electrode, irrespective of its polarity as mentioned earlier. With the third set in which both electrodes are thin and have the same dimensions, the glow phenomenon was observed at both the electrodes simultaneously at higher current densities. If the regions *A* and *B* are preheated, the glows at both the electrodes appear at relatively lower current densities. Similar conclusions were obtained by arranging the electrodes in the end-on positions in a single beaker cell. However, at no time a complete break down of the electrolytic medium was observed.

In order to study the polarizing effects at the electrode surface, platinum wires, one of diameter 0.3mm and length 0.85cm and the other of diameter 0.3mm and length 1.58 cm were used as electrodes. These electrodes were

immersed in NaOH solution of 0.5M strength. Power input for the onset of a continuous glow was found to be about 108 watts when the electrodes were clean. After platinizing them the input power required was found to be increased to 300 watts.

II. *Spectroscopic studies*

Platinum and tungsten wires of diameter 0.5 mm and copper and aluminium rods of diameter 0.56 cm were used as electrodes in this investigation. The experimental procedure for the excitation of the glow was the same as described earlier in section I(a). The colour of the glow was found to be yellowish in NaOH solutions and reddish in $CaCl_2$ solutions. The glow at the cathode was more intense and characterized by sputtering and hissing. A vapour sheath was seen to surround the glowing electrode and at higher input voltages it exhibited a sort of vortex motion. The intensity of the glow at the anode was found to be weak as compared to that at the cathode. The region surrounding the anode was also found to be comparatively quiet.

Typical spectra of the anode and cathode glows are shown in figures 4a to 4g (plates 3A—3B and 4A—4B). Figure 4a shows the anode glow spectrum which occurs in the form of a continuum in the region λ4870A to λ3990A along with superimposed atomic lines of calcium. The spectrum was recorded on the medium quartz spectrograph. Iron arc spectrum as well as hydrogen discharge tube spectrum were also recorded for comparision and identification of the glow lines. No atomic hydrogen lines are seen in this glow spectrum.

The spectra of cathode glows, displayed in figures 4b and 4c, were recorded on a low dispersion, constant deviation glass prism spectrograph. In figure 4b, the central spectrum is due to a hydrogen discharge tube for comparison. While one of the spectrum is due to cathode glow at a platinum electrode in NaOH solution the other is in $CaCl_2$ solution. These two glow spectra clearly exhibit persistent atomic lines of the metal ions present in the electrolyte. A faint atomic line of the electrode is also visible in one spectrum. Again the atomic hydrogen lines are not seen in both the glow spectra. Figure 4c exhibits two cathode glow spectra in NaOH solution, one at an aluminium electrode and the other at a copper electrode. It is observed that along with prominent sodium lines, the atomic lines of the metal electrodes are visible and some impurity lines have also appeared.

The cathode glow spectra exhibited in figures 4d to 4g have been recorded on the medium quartz spectrograph. Figure 4d clearly exhibits the existence of the OH bands along with the atomic lines of sodium

and copper in the case of the cathode glow at a copper electrode in NaOH solution In figure 4e are seen the NaH bands in the region λ3380A to λ4670A in addition to the OH bands In figure 4f is seen the general luminescence intensity distribution in the form of a structureless broad band in the region λ3700A to λ4700A at a copper cathode in $CaCl_2$ solution, in addition to the OH bands Figure 4g clearly exhibits OH bands in cathode glows in both, $CaCl_2$ and NaOH solutions along with prominent atomic lines

III *Oscillographic studies*

The development of the random pulses, during the glow phenomenon, as superimposed on the A C cycle, is shown in the oscillographic traces in figures 5a to 5e The voltage scale for the C R O screen used for these traces was 0 2 volts/cm The A C input voltage for the electrolytic cell was adjusted, consecutively at 2,10,18,38 and 40 volts for these traecs , the electrode in these studies was a copper wire of diameter 1 5 mm In figure 5f is seen the fully developed pulse pattern when a continuous glow was visible at a copper wire electrode of diameter 0 5 mm at 40 volts A C input. Figure 5g depicts a similar situation at a platinum wire electrode of diameter 0 3 mm at 45 volts A C input

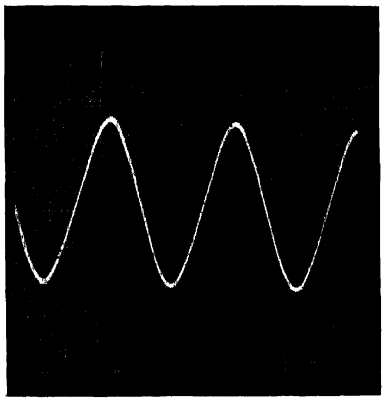


Figure 5a Oscillographic trace

Discussion

The electrolytic process leading to a luminescent glow at a wire electrode in aqueous solution is best depicted by the curve shown in

figure 3. A similar curve has been previously obtained by Hickling & Ingram (1964) also. The region AB of the curve indicates conven-

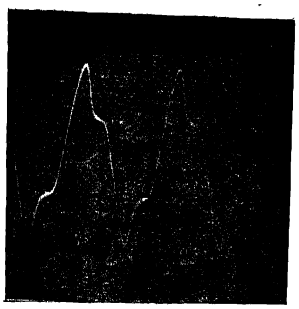


Figure 5b

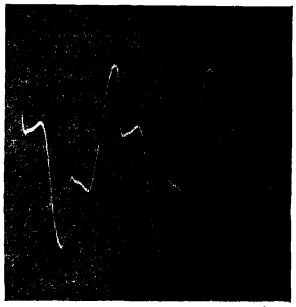
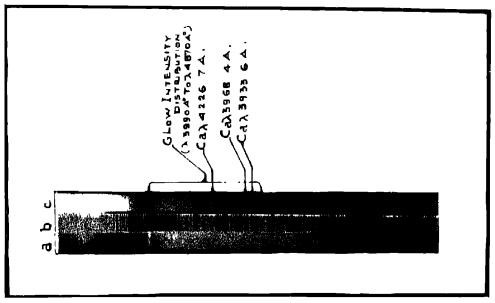


Figure 5c

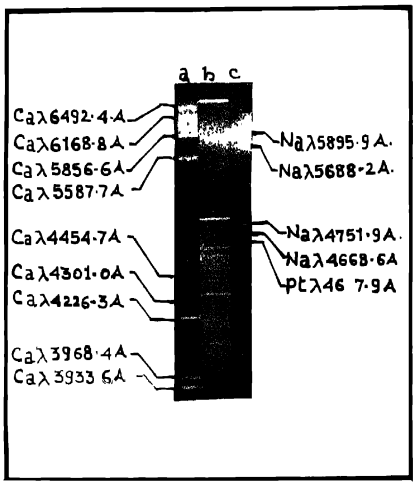
tional faradaic electrolysis. Due to the increase in the applied voltage the rate of gas evolution exceeds the rate of migration of the ions and the charge transfer processes at the electrodes are obstructed. At this stage, as mentioned earlier, the ammeter and the voltmeter pointer fluctuate within wide limits and then the current through the cell circuit falls, as indicated by the broken line BC. Further increase in the supply voltage results in the formation of a very thin and mobile vapour film around the thinner wire electrode. This film periodically collapses at some points, permitting the electrolyte to touch the electrode



Anode glow
Solution : $CaCl_2$
Anode . Platinum.

a :- Hydrogen spectra
b :- Iron spectra
c :- $CaCl_2$ Sol. spectra

Figure. 4a

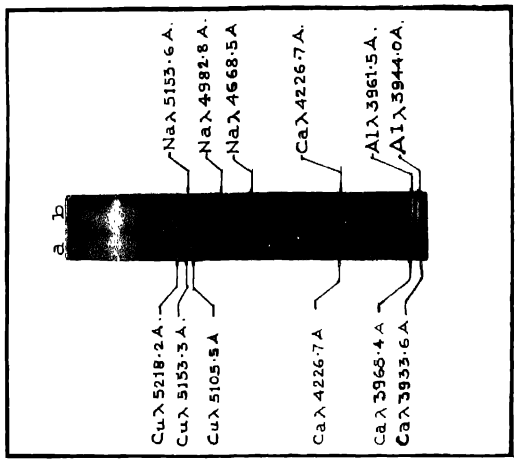


Solution: $CaCl_2$ (a) Cathode Platinum

(b) Hydrogen Tube spectra

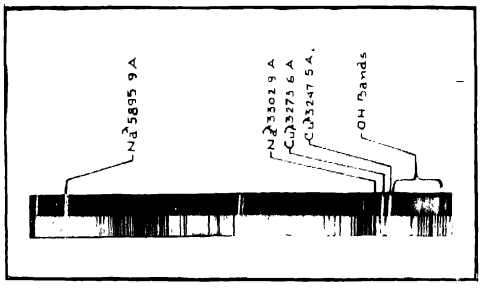
Solution : NaOH (c) Cathode : Platinum

Figure. 4b



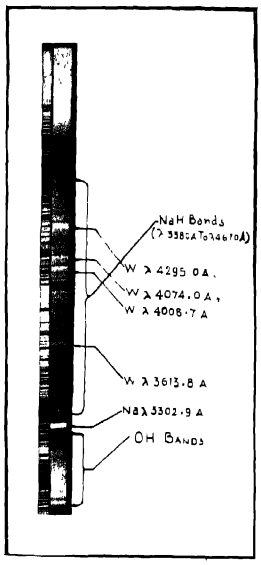
Solution :- NaOH Cathode: - (a) Copper
(b) Aluminium

Figure. 4c



Solution:- NaOH Cathode ; Copper rod.

Figure. 4d

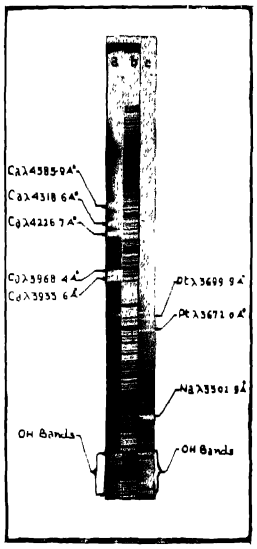


Solution: NaOH Cathode . Tungsten

Figure. 4e

a . Solution: $CaCl_2$ Cathode . Copper
b : Iron Arc

Figure. 4f



a. Solution : $CaCl_2$
Cathode : Platinum
b . Iron Arc
c : Soution · $NaOH$
Cathode : Platinum

Figure 4g

surface at those points. This results in a surge of current which produces local heating at the electrode surface and also visible spark-over. The local

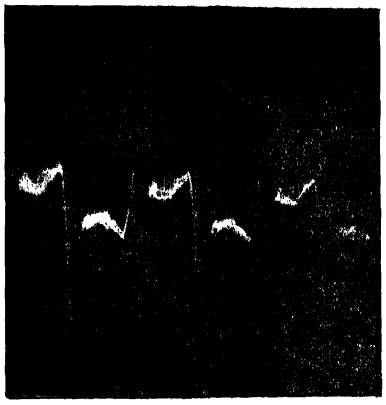


Figure 5d

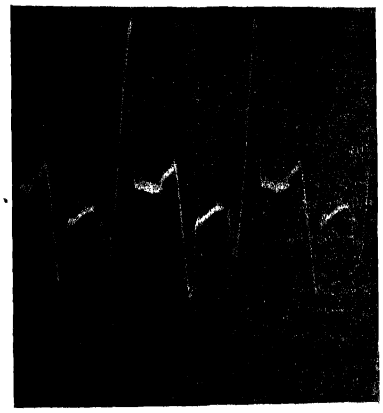


Figure 5e

heating process then forces out a vapour jet and the neighbouring liquid molecules rush there to take its place. The corresponding voltage-current

relation, representing this situation, is depicted by the region *OD* of the curve. At the point *D* the violent gas evolution ceases. The voltage-current

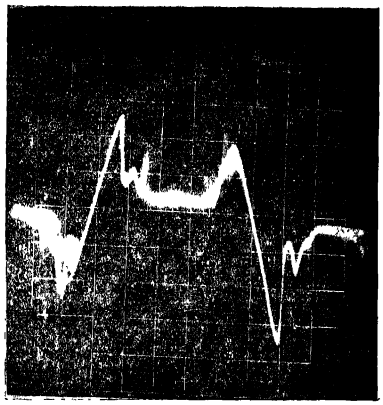


Figure 5f

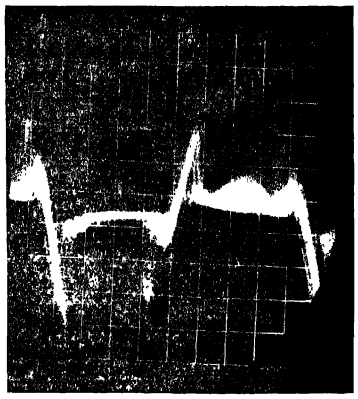


Figure 6g

readings are then stabilized. This situation is indicative of the formation of a stable superheated insulating layer around the electrode. It is at this stage that a continuous glow at the electrode appears. As the supply voltage is still further increased, the intensity of the glow increases monotonously with the current. The discharge of accumulated ions through the insulating layer, resulting into a visible glow, can be pictured as corona discharge.

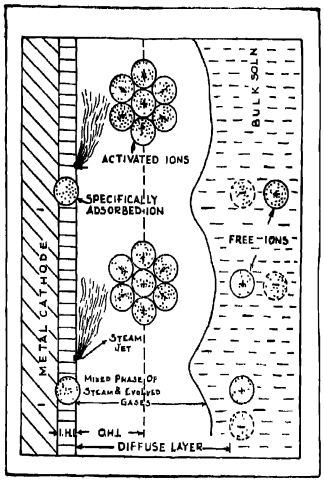


Figure 6. Qualitative model for the insulating thermal layer formed under glow conditions.

It is thus quite obvious that the superheated insulating layer around the electrode is the governing factor responsible for the glow. It is interesting to mention here that such insulating layers have been visualized in some other branches of physics and chemistry also. This layer seems to be of particular importance in the electro-hydro-dynamic (EHD) techniques (Markels & Durfee 1968). Recently one of us (Edkie 1969) has discussed the heat transfer mechanism under the influence of applied electric fields, using the concept of such an insulating thermal layer. Mohilner (1966) has shown that electric double layer has an important role in the kinetics of the faradaic and non-faradaic processes simultaneously taking place at a charge transfer electrode. A qualitative sketch of the situation existing near the electrode in the

present experimental conditions is given in figure 6. This figure is more or less similar to the double layer picture given by Mohilner. The inner Helmholtz layer (I.H.L.), surrounding the electrode is made of a stagnant, superheated, thin layer of water molecules. The outer Helmholtz layer (O.H.L.) consists of a mixed phase of electrolytically evolved gases and steam. This layer is followed by a diffused layer consisting of excited atoms, ions and radicals. In what follows, it is shown that the results obtained in the present investigations can very well be explained with the help of figure 6.

The dimensions of the insulating layer surrounding a short and thin electrode would obviously be very small as compared to the layer surrounding a thicker electrode. When the layer is thin, the input power required for the production of the glow is small because of the ease with which the required charge across the insulating layer builds up and the discharge takes place. The effect of platinizing the electrode is to increase the effective surface area of the electrode and the corresponding input power for the production of the glow is therefore larger. If the temperature of the electrolyte is elevated, the charge build up process is further accelerated and the discharge takes place with greater ease.

The anode glow spectrum, shown in figure 4a, exhibits a continuum along with few atomic lines of the alkali metal ions present in the electrolyte but does not show the atomic lines of the anode material nor any band structure because the heat in the anode layer is primarily dissipated towards the solution side and hence the anode material and other electro-active species, surrounding the anode, are not sufficiently excited. In figures 4b to 4g the cathode glow spectra exhibit the atomic lines of the cathode material because the heat in the cathode layer is primarily dissipated on the cathode itself. The absence of atomic hydrogen lines in all the spectra shows that free hydrogen atoms do not exist in the insulating layer. This may be due to the large interaction between the hydrogen ions and the water molecules. The hydrogen atoms are probably adsorbed on the electrode surface by means of valency bonds as pointed out by Potter (1961). Since steam is invariably present in the cathode layer, the OH bands are seen in the cathode glow spectra of both NaOH and $CaCl_2$ solutions. Under favourable conditions, some hydride bands, as in figures 4e and 4g, and some structureless broad bands, as in figure 4f, are seen. These bands show that radical recombination processes are taking place within the insulating layer. This work thus supports the radical recombination reactions suggested by Chandross *et al* (1964, 1965). Palit

(1968) has also recently envisaged from magnetic studies of the glow the formation of ion radicals in the glow process.

The development of deformities in the A. C. wave form in figures 5a to 5c, can be attributed to the building-up of the insulating layer around the wire electrode. The layer build up process develops a sort of back e.m.f. in the cell circuit and consequently the voltage across the standard low resistance (R in figure 2) decreases. The random pulses, superimposed on the deformed A.C. wave form, shown in figures 5d and 5e represent the corona discharges of the accumulated charge through the raptured insulating layer. Similar situation, shown in figures 5f and 5g, is also exhibited by two other wire electrodes of different materials.

Conclusion

Although the present study has thrown some light on the mechanism of the electrode glow, this study is by no means complete, It will be worth while to undertake theoretical as well as rigorous experimental investigations of this pheomenon which may reveal the structure of the thermal boundary layers which are encountered in many heat transfer processes. It is likely that such studies may lead to useful applications in industry and technology.

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References

Chandross, E. A., & Visco, R. E. 1964 *J. Am. Chem. Soc.* **86**, 5350.
Chandross, E. A., Longworth, J. W., & Visco, R. E. 1965 *J. Am. Chem. Soc.* **87**, 3259.
Edkie, R. G. 1969 *Ind. J. Pure and Appl. Phys*, **7**, 67.
Hickling. A., & Ingram, M. D. 1964 *Trans. Faraday Soc.* **60**, 783.
1964 *J. Electroanal. Chem.* **8**, 65.
Ivey, H. F. 1963 *Electroluminescence and related effects*, Academic Press, N. Y
Kellogg. 1950 *J. Electrochem. Soc.* **97**, 133.
Kuwana, T. 1966 *Electroanalytical Chemistry*, Ed. Bard, A. J., Vol. I Marcel—Dekker Inc., N. Y.
Mande, C. & Edkie, R. G. 1968 *Indian J. Phys.*, **42**, 271.
Markels, Michael Jr. & Durfee, Robert L. 1968 *Chem. Engr. Prog.* Symposium Series, 'Heat transfer Seattle', **64**, 67.
Mohliner, D. M. 1966 *Electroanalytical Chemistry*, Vol I., Ed. Bard, A., J. Marcel—Dekker Inc., N. Y.
Palit, S. R. 1967 *Indian J. Phys*, **41**, 622.
1968 *Indian J. Phys.*, **42**, 414.
Potter, E. C. 1961 *Electrochemistry*, Cleaver-Hume Press Ltd., London.